Unexpected Interaction between PEDOT and Phosphonium Ionic Liquids

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Ⓢ Supporting Information

ABSTRACT: In-situ-polymerized films of poly(3,4-ethylene-dioxythiophene) (PEDOT) are known to be relatively ordered materials and maintain this order under changing chemical and electrochemical conditions. It is therefore surprising that certain ionic liquids (ILs) were found to interact with PEDOT and thereby to a large extent disrupt the ordered structure. The current work demonstrates the expansion of the interlayer distance (d_{100}) of PEDOT and the composite of PEDOT with poly(ethyleneglycol) (PEDOT(PTS):PEG) in the presence of IL mixtures containing triisobutylmethylphosphonium tosylate (P_{1444}PTS) and water. In presence of the mixtures, the PEDOT(PTS):PEG film expands up to ∼100% while the PEDOT(PTS) film expanded ∼50%. The expansion did not increase the electrical resistance but increased the absorption in the $\pi-\pi*$ range, which can be explained by increased shielding of the PEDOT chains by the IL. The incorporation of P_{1444}PTS increased the capacitance by 350%, compared to the theoretical capacitance of PEDOT(PTS), due to the formation of additional double-layer capacitance.
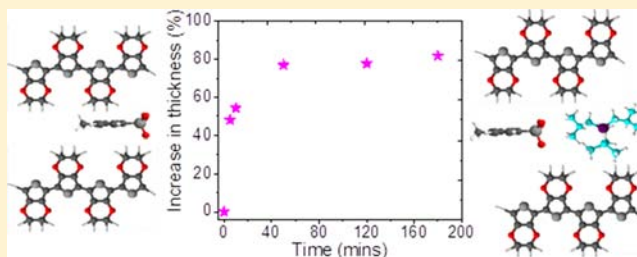
INTRODUCTION

Chemical in situ polymerization of poly(3,4-ethylenedioxy-thiophene) (PEDOT)-based thin films has been known to produce ordered and stable materials. Inganäs and co-workers[1,2] were the first to determine the structure of PEDOT with tosylate as a counterion using grazing-incidence small-angle X-ray diffraction techniques. They have shown that PEDOT(PTS) has an orthorhombic structure with lattice parameters a = 14 Å, b = 6.8 Å, and c = 7.8 Å, where a is the interlayer distance d_{100} and $b/2$ is the $\pi-\pi$ stacking (d_{020}). PEDOT(PTS) has been considered to be very stable when exposed to various solvents as well as when the oxidation state is changed during the electrochemical doping and dedoping of the material.[2] It was shown that the doped system has a more well-defined structural order than the dedoped system.[2] However, disruption of the ordered structure has only been seen in the solid–solid phase transition of PEDOT when the polymer was heated to 140 °C, due to the disappearance of the long-range π stacking order.[3] King and co-workers[4] have observed similar behavior during the heat treatment of PEDOT film with different counterions than tosylate. They have also investigated the effect of varying the counterions on the morphology of PEDOT and concluded that with smaller counterions a more regular structure is obtained rather than with bigger polyanions such as poly(styrene sulfonate) (PSS).

Ionic liquids (ILs) have been used for the electro-polymerization of CPs and as electrolytes for electrochemical devices.[5,6] The ability of ILs to swell and in many cases dissolve polymeric materials like cellulose has been widely reported.[7]

Izak and co-workers[8] demonstrated the swelling of polymeric membranes such as Nafion in 50 wt %/50 wt % C_4mimBF$_4$/H_2O at room temperature. They assumed that the ionic liquid cation is solvated by the water molecules and that the mixture forms clusters that expand the Nafion network.

Plesse et al.[9] studied the swelling kinetics of polybutadiene/poly(ethylene oxide) (PB/PEO) in C_2mimNTf$_2$. They showed that, without the presence of PEO, nothing occurred, and in the presence of 80% PEO, the uptake of C_2mimNTf$_2$ reached 200 wt %.

The interaction between ILs and the commercial PEDOT-(PSS) has been studied by several research groups. Recently, Badre et al.[10] demonstrated an enhancement on the conductivity of PEDOT(PSS) by using 1-ethyl-3-methyl-imidazolium tetracyanoborate (C_2mimB(CN)$_4$) as an additive. They reported a conductivity of 2084 S cm^{-1} after addition of 1.57 wt % of C_2mim B(CN)$_4$ and attributed the increase to the phase separation of PSS that results from a structural change in the film. Dobbelin et al.[11,12] investigated the effect of a variety of ionic liquids on PEDOT(PSS). They demonstrated that an improvement in electrical conductivity of the film is obtained with addition of about 50 wt % ILs due to the swelling of the amorphous PSS domains. These papers' main focus was the commercial PEDOT(PSS) film where they noticed an enhancement on the electrical conductivity.

Swelling of vapor-phase-polymerized (VPP) PEDOT(PTS) in molecular solvents was reported by Sirimanne et al.[13] It was shown that PEDOT(PTS) film swelled to 15% after 1 h in acetonitrile and further to a maximum of 36% after 16 h. The swelling of PEDOT(PTS) and PEDOT(PTS):PEG in water has been reported to be 23 and 26%, respectively.[14]

This paper investigates the effect of phosphonium-based ionic liquid on PEDOT(PTS) and PEDOT(PTS):PEG films prepared by vapor-phase polymerization using different techniques that gives an insight on the structural change of the conducting polymer. Interestingly, synchrotron X-ray diffraction measurements show that the $P_{1444}PTS/H_2O$ mixture disrupts the ordered phase of the PEDOT structure. It is the first time that such behavior is observed as it is well-known that solvents tend to first swell the amorphous phase before disrupting the ordered phase, often thereby leading to the dissolution of the material.

■ EXPERIMENTAL SECTION

Triisobutylmethylphosphonium tosylate ($P_{1444}PTS$) was obtained from Cytec. EDOT monomer, poly(ethylene gylcol) (PEG), and pyridine were purchased from Sigma Aldrich. All the chemicals were used without any further purification. The different ratio of the electrolyte is obtained by measuring the mass of the $P_{1444}PTS$ and H_2O.

PEDOT(PTS) films were synthesized by vapor-phase polymerization as previously reported.[15] The film thickness was measured using a Dektak 150 (Veeco) profilometer. The film thickness without the ionic liquid was initially measured and then measured immediately after adding a drop of the $P_{1444}PTS/H_2O$ mixture on the polymer film. The film thickness was measured over time.

Synchrotron X-ray scattering was performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 (2D scattering with an area detector, MAR345 image plate, at grazing incidence), with an incident energy of 12.7 keV. Scattering data are expressed as a function of the scattering vector $q = 4\pi/\lambda \sin\theta$, where θ is half the scattering angle and λ is the wavelength of the incident radiation. Here, q_{xy} (q_z) is the component of the scattering vector parallel (perpendicular) to the substrate. X-ray scattering measurements were performed under He atmosphere to reduce air scattering and beam damage to the sample.

UV spectroscopy of the PEDOT:PEG film was measured using a Jasco V-670 spectrophotometer.

The structures were optimized using Kohn−Sham density functional theory at the B3LYP/6-31+G* level using the NWChem software package. The starting geometries were varied in order to find the global minimum. Volumes were calculated using JMol for the Connolly surface at a distance of 0.25 Å from the Batsanov van der Waals radii of the atoms.

The capacitance measurements of the polymers were measured using cyclic voltammetry in an aqueous system containing 0.1 M Na PTS and in the ionic liquid system ($P_{1444}PTS/H_2O$, 5:5). Cyclic voltammetry was performed on a VMP2 multichannel potentiostat. A three-electrode setup was used with titanium mesh as the counter electrode, a platinum wire as the reference electrode, and a PEDOT(PTS):PEG film coated on FTO as the working electrode.

The swelling of PEDOT(PTS):PEG films in aqueous medium was measured using a quartz crystal microbalance (QCM 200 from Stanford Research System). PEDOT(PTS):PEG was polymerized on the QCM crystal and then exposed to the aqueous electrolyte. The changes in frequency were used to calculate the percentage of mass uptake.

The sheet resistance was measured by applying a technique used by Winther-Jensen and co-workers.[16] DC measurement was performed to avoid contribution from the ionic liquid and aqueous electrolytes. Three different electrodes were used in each electrolyte in order to obtain the standard deviation on the measurement.

■ RESULTS AND DISCUSSION

Previously, we have demonstrated that the electrodeposition of metallic and semiconducting nanoparticles from a phosphonium ionic liquid electrolyte *inside* the composite polymer PEDOT:PEG occurred with a significant increase in film thickness.[15] These observations called for a more in-depth investigation of the interaction between VPP PEDOT(PTS) and the phosphonium ionic liquid. The changes in PEDOT-(PTS) and PEDOT(PTS):PEG film thicknesses were first measured in a series of ionic liquid/water mixtures as well as in pure water. Figure 1 shows the percentage increase in thickness
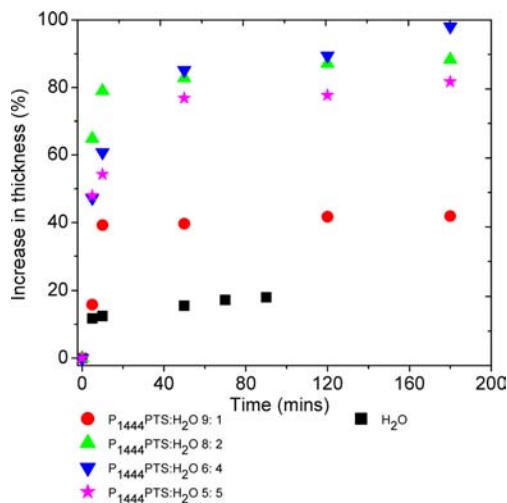

Figure 1. Increase in thickness of PEDOT(PTS):PEG films as a function of time in different concentrations of ionic liquids.

of PEDOT(PTS):PEG over time in different concentrations of ionic liquids. The increase in thickness is greatly influenced by the ratio between $P_{1444}PTS$ and water. The largest change occurred in the 6:4 ratio of ionic liquid/water mixture and reached a maximum of 98 vol % change in film thickness after 180 min. As a general trend, the thickness increased over 180 min with higher amount of water and reached a maximum for the mass ratio of 6:4 and then dropped down to 82 vol % increase for the 5:5 ratio. In the case of pure water, the PEDOT(PTS):PEG film swelled only by 18% after 90 min. This range of swelling for PEDOT(PTS):PEG in pure water was confirmed by using the QCM measurement for the PEDOT(PTS):PEG film: an increase in mass of 22% was obtained after 24 h.

Unfortunately, the QCM measurements could not be performed with the ionic liquid electrolytes due to the high viscosity of the IL. Interestingly, the change in thickness of the PEDOT(PTS) film is not as significant as the PEDOT-(PTS):PEG film (see Supporting Information, Figure S1). For the 5:5 IL/water ratio, the change in thickness only reached a maximum of 40 vol % over the 180 min. This indicates that the PEG part of the composite material is increasing the speed of the swelling as well as absorbing significant amounts of IL. This is in good agreement with previous reports on swelling of PEG in various ILs.[9]

In Figure 2, the absorbance (at 545 nm) of the PEDOT-(PTS):PEG film is compared to the percentage increase in thickness of the film in the $P_{1444}PTS/H_2O$ (5:5) electrolyte (for full UV−vis spectra, please see Supporting Information Figure S2). The inset shows the color change occurring during
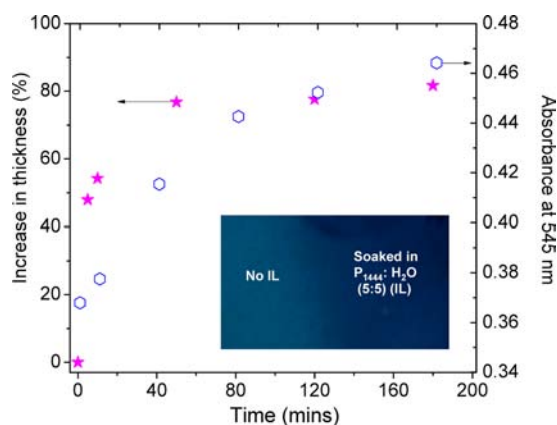
Figure 2. Absorbance at 545 nm and swelling of PEDOT(PTS):PEG film in the $P_{1444}PTS/H_2O$ (5:5) electrolyte over time.

exposure of the film in the IL electrolyte. As observed in Figure 2, the increase in film thickness is reflected in the increase in absorbance (at 545 nm) of the polymer film. The absorption peak formed at lower wavelength (545 nm in this case) is usually attributed to the $\pi-\pi^*$ transition band, which corresponded to the neutral form of PEDOT(PTS).[17,18] In the experiment described above, no reducing potential was applied to the system; that is, we were not attempting to change the oxidation state of the polymer film.

As a control experiment, the film resistance was measured in order to investigate if the ionic liquids would cause an increase in resistance as could be expected from the occurrence of the $\pi-\pi^*$ transition band, which traditionally is assigned to the neutral (less conducting) form of PEDOT(PTS). In Figure 3,
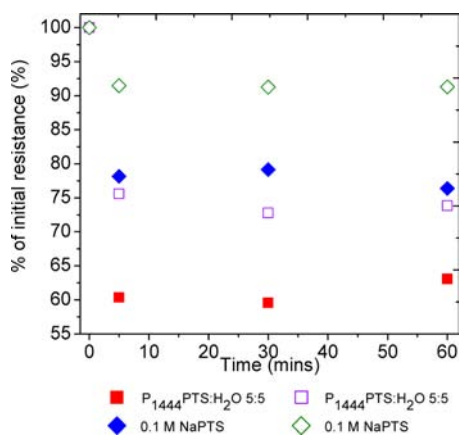

Figure 3. Resistance of PEDOT(PTS):PEG (filled point) and PEDOT(PTS) (unfilled points) films in 0.1 M NaPTS and $P_{1444}PTS/H_2O$ (5:5).

the change in the sheet resistance over time for the PEDOT(PTS):PEG and PEDOT(PTS) films is shown for immersion in 0.1 M NaPTS and in $P_{1444}PTS/H_2O$ mixture. The initial sheet resistance of the PEDOT(PTS):PEG film before being immersed into the $P_{1444}PTS/H_2O$ mixture and in 0.1 M Na PTS is 60.4 and 63.2 Ω/sq, respectively, and in the case of PEDOT(PTS) film, the sheet resistance was 54.6 Ω/sq prior to immersion in the IL mixture and 51 Ω/sq prior to immersion in 0.1 M Na PTS. Addition of an organic solvent to PEDOT(PSS) is known to increase the conductance of the materials by several orders of magnitude.[19,20] However, with

VPP PEDOT(PTS), no such significant change is normally observed for traditional electrolytes. In the present case, no unexpected change in the resistance of the PEDOT(PTS):PEG and PEDOT(PTS) films in either electrolytes was observed, and the sheet resistance of the film remains stable over time in both PEDOT(PTS) and PEDOT(PTS):PEG films after addition of the electrolytes. This confirms that no change in the oxidation state (i.e., reduction) occurred when the films were exposed to the IL or Na PTS electrolyte.

One possible explanation for the increased absorption of the $\pi-\pi^*$ transition band is that the IL is permeating the PEDOT(PTS):PEG film over time, as demonstrated in Figure 1, thereby expanding the interchain distances far enough to shield the individual PEDOT(PTS) chains. By shielding a certain part of the polymer chain, we are removing the possibilities of having multiple polaronic levels; therefore, the absorption spectrum of the PEDOT(PTS) film is changing because it is depending on the possible electronic transitions in the polymer, and the absorption in the HOMO−LUMO range is getting more pronounced without causing any change in the oxidation state of the polymer film. Beljonne et al.[21] demonstrated a similar behavior for poly(para-phenylene-vinylene) experimentally and by simulations, where they showed that the polymer can have different polaronic excitation depending on the chain lengths (and thereby possible interaction between conjugated segments) leading to a change in the absorption spectra of the polymer (i.e., the appearance of new intense optical transition at lower wavelength). Further, it is worth noticing that the bipolaron absorption (at ~1200 nm) decreases accompanied by an increase in polaron absorption (at ~850 nm) during the exposure to IL/water mixtures (see Supporting Information Figure S1). This change would normally be attributed to a lower oxidation state but can, in a way similar to the change in the $\pi-\pi^*$ absorption, be explained by the increased shielding of individual PEDOT chains in the presence of IL within the material.

To further understand the influence of the $P_{1444}PTS$ on the order of PEDOT(PTS) and PEDOT(PTS):PEG, synchrotron X-ray diffraction was performed on films before and after soaking in IL/water mixtures. The X-ray diffraction pattern (Figure 4A,B) clearly shows that a change in the ordered structure of the PEDOT(PTS):PEG film occurs after soaking the film in $P_{1444}PTS$. Aasmundtveit and co-workers[2] previously proposed a molecular structure of PEDOT(PTS) using grazing-incidence small-angle X-ray diffraction. The two main lattice parameters of the PEDOT(PTS) film are the $\pi-\pi$ stacking (d_{020}) and the interlayer distance d_{100} (see Figure 5). Figure 4C shows a slice of the 2D grazing-incidence data that describes scattered intensity near the surface normal, $\sim q_z$ (from Figure 4A,B) for the as-prepared films,[2,22] as well as the IL-soaked films (scattering from the IL alone is shown as a reference). Similar data are presented for the grazing portion of the scattering (q_{xy}) in Figure 4D. The signal from the IL-soaked film is convoluted with the scattering from the IL, but peak positions for the PEDOT(PTS) assemblies can be extracted by peak fitting. In all cases, the scattering from the PEDOT(PTS) loses significant intensity upon IL exposure, and the (100) planes undergo expansion after soaking in IL.

Table 1 shows a ~1 Å increase in d_{100} and a reduction in the coherence length from 62 to 52 Å, indicating a decrease in crystallite size and/or ordering along this crystallographic direction.[23]
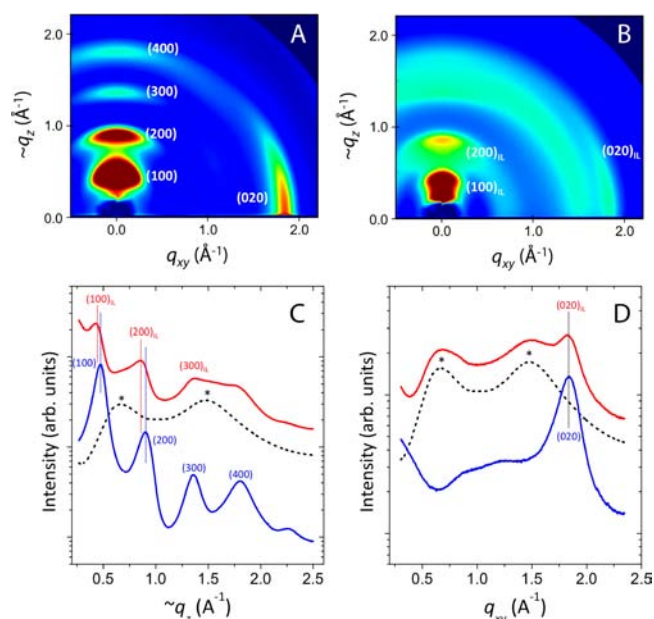

Figure 4. X-ray scattering of PEDOT(PTS):PEG films. Two-dimensional GIXD of (A) as-prepared PEDOT(PTS):PEG and (B) IL-soaked PEDOT(PTS):PEG films. Intensity profiles from A,B: (C) specular and (D) grazing incidence of as-prepared PEDOT(PTS):PEG films (blue), IL-soaked films (red). As a reference, the scattering from the ionic liquid is shown as a black dotted line, and the IL scattering peaks are labeled with "*". In C,D, the plots are shifted for clarity.

Table 1. Interplanar Spacings and Coherence Lengths Extracted for the Lamellar Stacking (100) and π Stacking (020) of As-Prepared PEDOT:PEG, after IL Soaking, and after Rinsing/Soaking in DI Water (Showing Reversibility)[a]

	d_{100} (Å)	L_{100} (Å)	d_{020} (Å)[b]	L (Å)
as-prepared	13.3	62	3.41	41
IL soak	14.5	52	3.41	39
DI H_2O soak/dry	13.3	59	3.41	38

[a]Values are estimates extracted from 2D GIXD data in Figure 4 and Supporting Information Figure S3. [b]The π–π stacking distance $b/2$.

The change in the coherence length (L_{100}) shows that the IL is not only expanding the polymer film but also causing some changes in the crystalline fraction of the polymer structure, that is, disrupting some of the ordered phase of the polymer film. The spacings and coherence of the π stacking (020) remain largely unchanged upon IL soaking. The microstructural changes described here are reversible upon rinsing the IL-soaked films in DI water and drying them on a hot plate (see Table 1).

The reason for the observed microstructural changes may be due to the intercalation of the $P_{1444}PTS$ in the interlayer of the PEDOT(PTS):PTS crystallites, where it forces the (100) layers apart. The radius of the P_{1444} cation was calculated to be 4.0 Å, while the radius of the PTS anion is reported to be 2.9 Å.[24] The difference between these ions is about 1.1 Å, which corresponds approximately to the difference in d_{100} spacing between the as-prepared film and the IL-soaked film (Table 1). This expansion and disruption of the crystalline structure likely accounts for the smaller swelling in the PEDOT(PTS) films, and such expansion along with IL swelling in the PEG phase accounts for the near 100% swelling observed in PEDOT(PTS):PEG films (Figure 1).

Figure 5 shows a schematic diagram that illustrates the role of the $P_{1444}PTS/H_2O$ mixture in the swelling of the PEDOT-
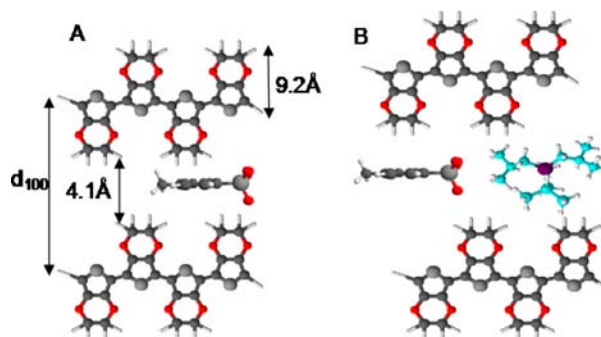

Figure 5. Schematic diagram of the intercalation of $P_{1444}PTS$ inside PEDOT(PTS) crystallites; (A) schematic structure of PEDOT(PTS) without IL and (B) with $P_{1444}PTS$.

(PTS) crystallites within a film. It is quite interesting that a simple IL can increase/disrupt the interlayer distance d_{100} as observed in Figure 4. The $P_{1444}PTS$ is thus thought to be intercalated in the interlayer distance d_{100} of PEDOT(PTS).

If PEDOT(PTS) has the ability to allow the insertion of counterions in the film and also IL into the PEDOT(PTS) crystallites, forming "layers" of IL, there exists a possibility to store charge in the surrounding electrical double layer as well as throughout the polymer network by rapid faradaic charge transfer also known as pseudocapacitance. For the past few years, a great deal of research on the use of PEDOT for electrochemical capacitors has been performed due to the huge demand of active materials with high specific capacitance (Figure 6). Cyclic voltammetry was therefore used to
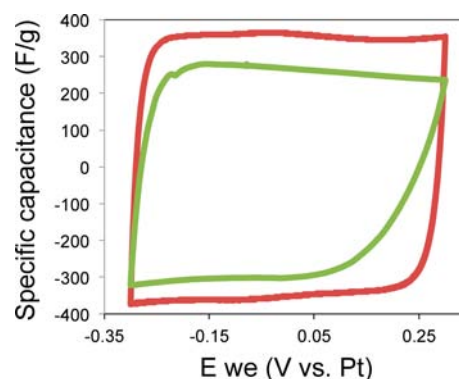

Figure 6. Specific capacitance of PEDOT(PTS):PEG in different electrolytes: 0.1 M NaPTS (green trace) and $P_{1444}PTS/H_2O$ (5:5) (red trace). Calculated from cyclic voltammograms, scan rate 20 mV s^{-1}.

investigate the capacitive behavior of PEDOT(PTS):PEG films when IL was introduced into the film. The cyclic voltammetry was performed in the potential range of −0.4 to 0.3 V at a scan rate of 20 mV s^{-1}. The theoretical maximum specific capacitance of pure PEDOT(PTS) is known to be about 200 F g^{-1}, which is determined by the unit molecular weight of the polymer (140 g mol^{-1}) and the doping level of counterions (0.3).[25] In our case, the specific capacitance of the PEDOT(PTS):PEG film in the ionic liquid electrolyte is 716 F g^{-1} (red curve) and in 0.1 M NaPTS (green curve) reached a value of 570 F g^{-1}. The high specific capacitance may also be

enhanced due to the presence of PEG that allows more facile diffusion of ions inside the polymer network as previously reported.[14] These values can be compared to reported capacitance of other PEDOT-containing pseudocapacitors, which is in the range of 325 F g^{-1} for specially designed PEDOT derivatives[26] and 427 F g^{-1} for ternary composites with MnO_2 and carbon nanotubes.[27]

CONCLUSION

We observed a distinctive swelling behavior of the conducting polymer PEDOT(PTS) in the presence of $P_{1444}PTS/H_2O$ mixtures. This swelling was accelerated in the composite with PEG. In water, the polymer film swelled only to a maximum of 18 vol %, whereas in the presence of the $P_{1444}PTS/H_2O$ mixture, the thickness of the film nearly doubled with the IL to water ratio of 6:4. The intercalation of the IL/water mixture into the PEDOT causes disruption of the ordered structure and a shielding of a certain segment of the polymer chains, leading to an increase in ("$\pi-\pi^*$") absorption at lower wavelengths. These changes occurred without any dedoping of the PEDOT(PTS) as the DC resistance remained constant or slightly decreased. The intercalation with IL also increased the specific capacitance of the PEDOT:PEG film explained by increased "area" where capacitive charge storage is possible.

The current study has only investigated a very small fraction of the ILs available, and among these, the $P_{1444}PTS$ reported showed the most significant interaction with PEDOT. Future studies will aim to find or develop even more suitable ILs for the interaction with PEDOT and other conjugated polymers as well as investigate the influence of temperature on the intercalation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The complete UV spectra of the effect of IL on the PEDOT:PEG film, the % increase in thickness with time of PEDOT film, the X-ray diffraction pattern and the 2D GIXD of the IL and as-prepared PEDOT:PEG film. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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